

Thermal analysis of the oxidation of natural graphite: isothermal kinetic studies

K. Zaghib^{a,*}, X. Song^b, K. Kinoshita^b

^aInstitut de Recherche d'Hydro-Québec, 1800 Boul. Lionel-Boulet, Varennes, Que., Canada J3X 1S1

^bEnvironmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Received 24 August 2000; accepted 8 December 2000

Abstract

The oxidation kinetics of natural graphite particles (2–40 μm average particle size) with a flake-like morphology were investigated at 933, 982 and 1033 K. The reaction rate in air increased with increase in temperature and with a decrease in particle size of natural graphite. The activation energy, derived from the classical Arrhenius relationship, was 188 ± 2.2 kJ/mol, in good agreement with published results. The activation energies of the natural graphite did not show any systematic trend with particle size. The rate constant, normalized for the area of active sites, is independent of the particle size and Brunauer–Emmet–Teller (BET) surface area, which strongly suggests that the edge sites play a significant role in the oxidation kinetics. This observation is consistent with conclusions reported in the literature that the oxidation kinetics of carbonaceous materials decreases with a decrease in active surface area. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermal analysis; Natural graphite; Oxidation

1. Introduction

The oxidation rate of carbonaceous materials in air is strongly dependent on parameters such as the surface area and crystallographic structure [1–3]. The crystallographic structure of carbon consists of distinct surface sites, i.e. basal plane and edge sites. Highly graphitized carbons have a preponderance of basal plane sites that are less reactive than disordered carbons that contain a larger fraction of edge or active sites. The concept of active sites for oxidation reactions involving oxygen chemisorption or gasification

of carbonaceous materials was reported in the studies by Rubak et al. [4], Radovic et al. [5], Laine et al. [6] and Coltharp and Hackerman [7]. Rubak et al. [4] concluded that the oxidation reaction of chars is proportional to the active surface area available for reaction and not the total surface area because chars that were heat treated had lower surface area and lower reactivity. Radovic et al. [5] suggested that the emergence of the (1 1 0) peak at $2\theta = 43^\circ$ in the X-ray diffraction (XRD) spectra of carbon is a strong indication of a decrease in the concentration of active sites. The emergence of the (1 1 0) peak shows the presence of a more graphitic carbon, which has a larger fraction of basal plane sites and a diminution of edge sites. Other researchers have reported the relative fraction of edge sites present on carbonaceous materials. The results indicate that the fraction of edge sites varied

* Corresponding author. Tel.: +1-450-652-8019;
fax: +1-450-652-8424.
E-mail address: karimz@ireq.ca (K. Zaghib).

widely with the structure and particle size. Barton and Harrison [8] calculated the edge and total surface area of graphite crystallite from the crystallite parameters, L_c and L_a , obtained from XRD analysis. They assumed crystallites of cylindrical shape with height L_c of 90 Å and diameter L_a of 300 Å. From this analysis, the total surface area is 160 m²/g and the edge plane area is 60 m²/g. In this example, the percentage of edge sites is 37.5%. Coltharp and Hackerman [7] reported that the percent of edge sites on a high-surface-area carbon black is 68% of the Brunauer–Emmet–Teller (BET) surface area (~110 m²/g). Such high percentages of edge sites are not likely to exist with large graphite particles that have dimensions greater than 1 µm. For example, Chung et al. [9] considered a circular disk as a representation of a graphite flake and calculated an edge fraction of ≈1% for particle diameter of 10 µm and thickness of 0.1 µm.

We recently presented results obtained by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) of natural graphite particles with a prismatic (flake-like) structure [10]. Three thermal parameters, ignition temperature (T_i), temperature maximum (T_m) in the DTA curves, and the temperature at which 15% carbon weight loss (T_{15}) is attained, were determined for a series of natural graphite samples (average particle size, 2–40 µm) using simultaneous TGA/DTA. The results support the observation that the fraction of edge sites has a strong influence on these thermal parameters for the oxidation of graphite.

The intent of this paper is to extend the oxidation studies to consider the role of edge sites on the oxidation kinetics of natural graphite particles with a flake-like morphology. An ideal prismatic structure served as a model for the natural graphite particles, and this model was used to determine the relative fraction of edge and basal plane sites associated the natural graphite particles [11]. The fraction of edge carbon atoms (f_e) in a flake-like structure was determined and expressed as a function of the crystallographic parameters of graphite:

$$f_e = \frac{(2B/L_a) + (T/d_{002})}{(2B/d_{100}) + (T/d_{002})} \quad (1)$$

where d_{100} is the in-plane lattice constant (2.4612 Å), d_{002} is the distance between the layer planes, L_a is size of the layer plane, B is the length of the basal

planes and T is the thickness of the edge planes. The area of edge sites (S_e) is calculated using Eq. (1)

$$S_e = f_e S \quad (2)$$

where S is the BET surface area of graphite.

2. Experimental details

Six samples of natural graphite powders with average particle size 2, 7, 12, 20, 30 and 40 µm were obtained from a commercial source. These samples, which will be designated NG2 to NG40, respectively, represent a wide range of particle sizes, but with similar particle morphology. The BET surface area was measured with a Quantachrome Autosorb automated gas sorption system using N₂ gas. XRD analysis (Siemens D500 Diffractometer) was used to determine the d_{002} spacing and the crystallite size, L_c . Scanning electron microscopy (SEM, Hitachi) was employed to determine the morphology and dimensions of the edge and basal plane. Details of the physical properties are presented elsewhere [10,11]. In brief, the BET surface area decreased from 12.1 to 2.3 m²/g with an increase in the average particle size of 2 to 40 µm. XRD analysis showed that the d_{002} spacing is 3.36 Å, and L_c ranges from 54 to 80 Å. The results obtained from Raman spectroscopy indicate L_a is in the range from 110 to 183 Å.

The thermal analysis experiments were conducted using an instrument capable of simultaneous TGA/DTA (SDT 2960, TA Instruments, Inc., New Castle, DE) to monitor both the weight change (balance sensitivity, 1 µg) and temperature change (ΔT sensitivity, 0.001°C) of the samples. The experimental procedure consisted of heating the sample in flowing nitrogen (99.999% purity, 100 cm³/min) at 10°C/min to 1200°C to eliminate any surface oxygen groups. Because the graphite samples were produced at temperatures above 1200°C, this heat-treatment step is not expected to change their crystallographic structure. The temperature was then lowered at 10°C/min to the desired temperature (933, 982 or 1033 K) for the isothermal oxidation studies. When the desired temperature was reached, the sample was held at that temperature for about 5 min and then the gas was switched from nitrogen to air. The weight loss during oxidation was monitored as a function of time. Preliminary

experiments were conducted to identify the appropriate mass of graphite required to maintain the oxidation reaction under kinetic control. These measurements indicated that the oxidation rate was not diffusion controlled with a sample weight of 5–10 mg.

A commercial software program (KaleidaGraph, Synergy Software, Reading, PA) was used to analyze and plot the experimental data. Because of the limited number of graphite samples, no attempt is made to present statistical information. The software program was used to show the trend of the data, and this is noted in several of the figure captions.

3. Discussion of results

3.1. Data analysis

The isothermal oxidation results were analyzed following the theoretical approach discussed by Radvic et al. [5]. The rate of graphite oxidation (R) is defined by the equation for reaction of a solid

$$R = - \left[\frac{1}{w_t} \right] \left[\frac{dw_t}{dt} \right] \quad (3)$$

where w_t is the mass of carbon at time t . The conversion of carbon, X , is given by

$$X = \left[\frac{w_0 - w_t}{w_0} \right] \quad (4)$$

where w_0 is the initial mass of carbon. Substituting the appropriate form of Eq. (4) in Eq. (3) yields

$$R = \left[\frac{1}{(1 - X)} \right] \left[\frac{dX_c}{dt} \right] \quad (5)$$

It was further assumed that the rate is a function of the concentration of carbon and has a pseudo-zero-order dependence on gas concentration

$$R = \left[\frac{1}{(1 - X)} \right] \left[\frac{dX_c}{dt} \right] = kC_a \quad (6)$$

where k is a rate constant and C_a is the concentration of carbon active sites. The rate constant is determined from the initial slope of the weight loss of carbon (i.e. at $X \rightarrow 0$) during the isothermal experiment

$$k = \frac{[dX_c/dt]_0}{C_a} \quad (7)$$

and normalized for the area of active sites. The value of C_a is assumed to be equal to S_c derived from Eq. (2).

3.2. Kinetic data

Representative examples of the isothermal kinetic data that were obtained with two natural graphite samples are presented in Fig. 1. The conversion of carbon was determined from the weight loss, as indicated in Eq. (4). It is apparent that the weight loss increases as the temperature increases and the particle size decreases, and this behavior was observed with each of the samples. The reaction rates (see Eq. (5)) were obtained from the initial slope of plots such as those shown in Fig. 1, and these results are plotted in Fig. 2 as a function of the particle size and oxidation temperature. Only the initial rates are considered in this analysis (i.e. $X \rightarrow 0$) because the particle morphology and relative fraction of edge sites at progressively higher X are unknown. For comparison, Lang and Magnier [12] reported that the oxidation rate for natural graphite ($3 \text{ m}^2/\text{g}$) in dry air at 893 K was 0.00025 min^{-1} , which is 1/4 that obtained with NG40 at 933 K (0.001 min^{-1}). The reaction rate increases with an increase in temperature and with a decrease in the particle size of natural graphite. The fact that the reaction rate is a function of particle size is the subject of major interest in this paper. As the particle size decreases, the surface area increases, which could be the contributing factor for the higher reaction rate. However, as discussed later, we believe that the area of the active sites rather than the total surface area is the important factor that determines the reaction rate.

The activation energy was derived from the classical Arrhenius relationship using the data in Fig. 2. These results are plotted in Fig. 3, along with the data for a synthetic graphite [13]. A software program was used to calculate the slope, from which an activation energy of $188 \pm 2.2 \text{ kJ/mol}$ was obtained for the natural graphite samples and 170 kJ/mol was found for the synthetic graphite (SG). The activation energies of the natural graphite did not show any systematic trend with average particle size. Therefore, only the average value is presented. The results obtained with the natural and synthetic graphites in Fig. 3 are in reasonably good agreement, but it is not appropriate to make further comparisons at this time because we do

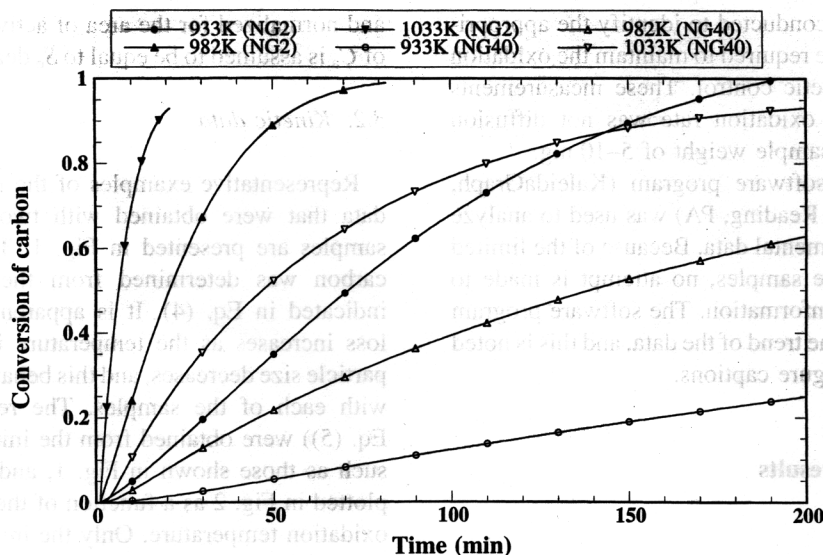


Fig. 1. Isothermal oxidation of natural graphite at 933, 982 and 1033 K. Solid symbol: NG2; open symbol: NG40.

not have any information on the physical properties of the synthetic graphite. Extending the comparison further, Radovic et al. [5] reported an activation energy of 200 kJ/mol for spectroscopically pure natural graphite (SP-1, Union Carbide Corp.), which is in good agreement with our result. As mentioned in Section 1, specific sites that are more active (e.g. edge sites) than other sites (e.g. basal

plane sites) are involved in the oxidation rate and reactivity of carbon. Following the conclusion of Radovic et al. [5], the “total surface area is not a relevant reactivity normalization parameter”, but rather it is the active surface area that is important. The analysis [10,11] of the fraction of edge sites presented an opportunity to further explore the role of active sites on the oxidation kinetics of flake-like

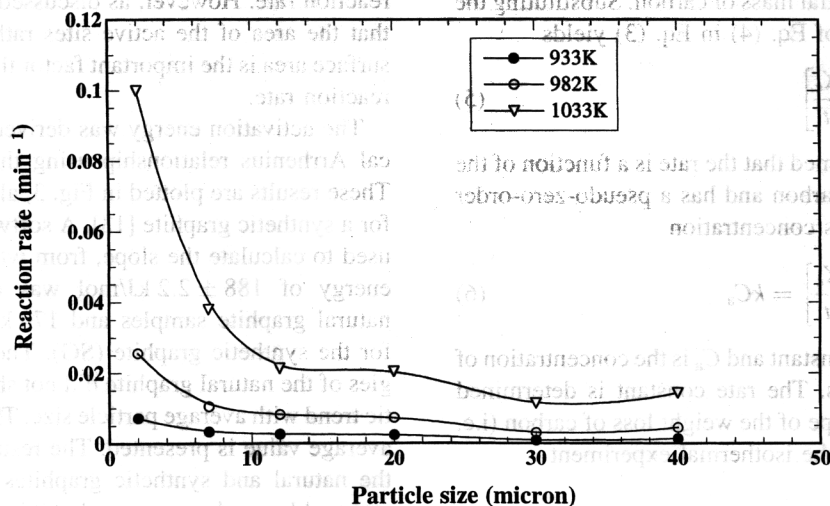


Fig. 2. Oxidation rate of natural graphite of various particle size at different temperatures.

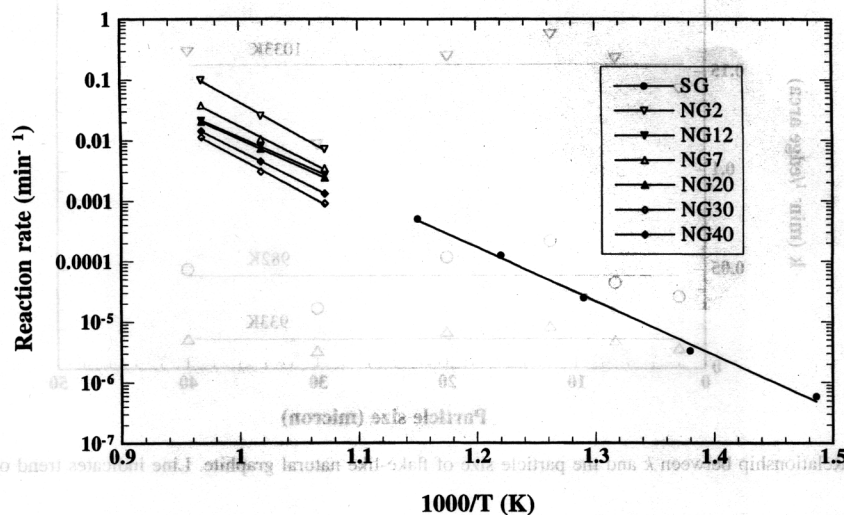


Fig. 3. Arrhenius relationship for isothermal oxidation of natural graphite and synthetic graphite (SG).

natural graphite. With this in mind, the rate constant k (Eq. (7)), which is normalized to the area of edge sites ($f_e S$) was analyzed. Fig. 4 shows the variation in the surface area of the edge sites, which was computed from Eq. (2), and BET surface area for the flake-like natural graphite with different average particle size. Both surface areas trend lower with an increase in the particle size. With these flake-like natural graphite, f_e varied from 0.06 to 0.03, and the surface area of the edge sites ranged from 0.7 to 0.09 m²/g. The results indicate that S_e represents only a small fraction of the

total surface area of the natural graphite particles. However, its role in the oxidation kinetics is significant.

The relationship between k and the particle size is presented in Fig. 5. The trend of the data suggests that k is independent of the particle size, but the reaction rate is not (see Fig. 3). However, the role of edge sites on the oxidation kinetics cannot be unequivocally understood from the trend in the data in Fig. 5. The plots in Fig. 6a show that the reaction rate increases linearly with the BET surface area. As the BET

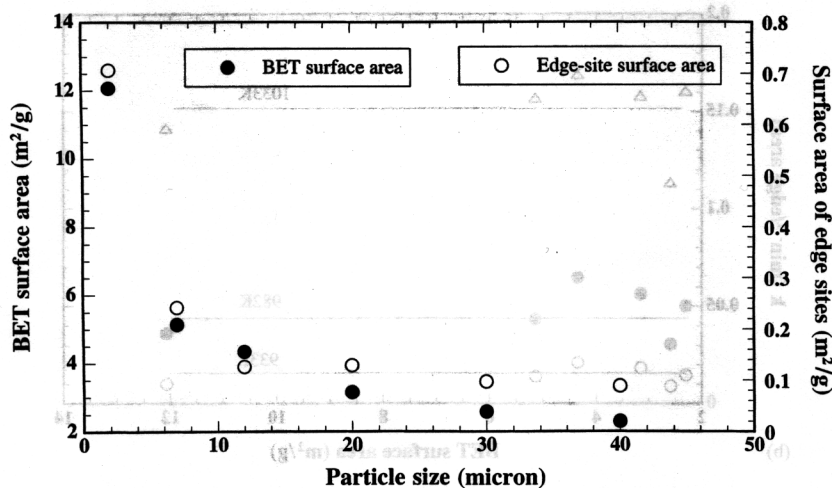


Fig. 4. Variation in BET surface area and edge-site surface area with particle size of flake-like natural graphite.

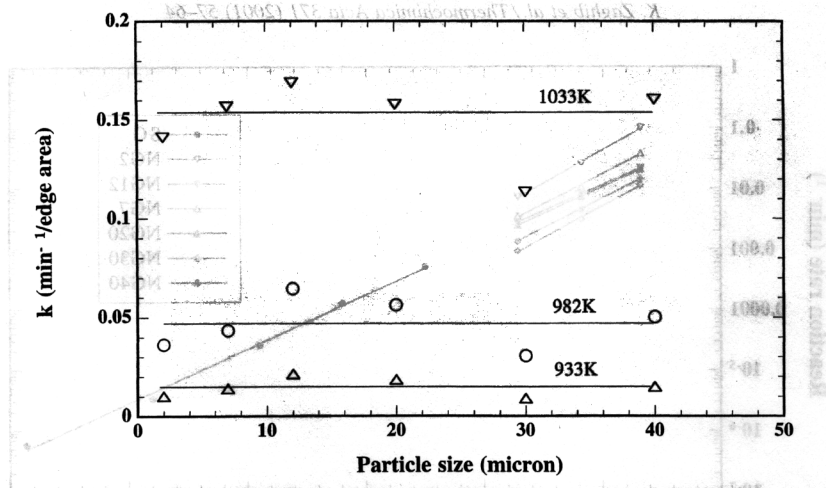
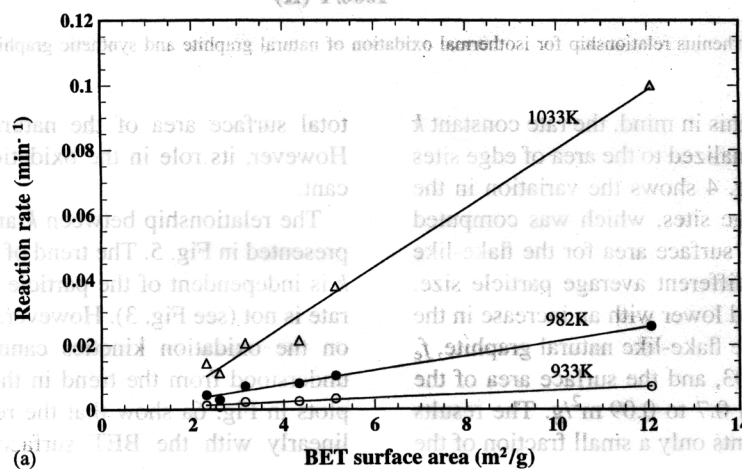
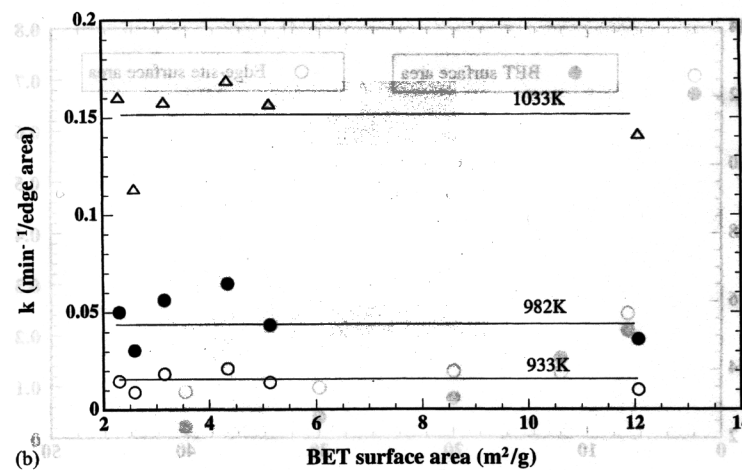


Fig. 5. Relationship between k and the particle size of flake-like natural graphite. Line indicates trend of data.



(a)



(b)

Fig. 6. Relationships between (a) R and BET surface area, and (b) k and BET surface area of flake-like natural graphite. Line indicates trend of data.

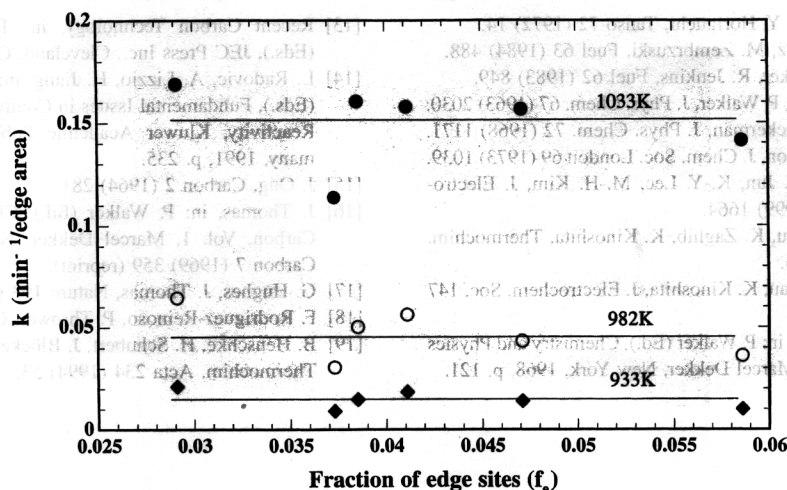


Fig. 7. Relationship between k and the fraction of edge sites on flake-like natural graphite. Line indicates trend of data.

surface area increases, the surface area associated with both the edge and basal plane sites also increases. Thus it is not easy to discern if the edge sites are playing a major role in the oxidation kinetics. When the oxidation reaction is assumed to occur mainly on the edge sites, and the kinetic data is normalized for the surface area of edge sites (k), the results for k as a function of the BET surface area in Fig. 6b are obtained. The trend lines suggest that k is constant, independent of the BET surface area. This trend is expected for oxidation reactions that are correlated to the surface area of the edge sites. Analysis of the relationship between k and the fraction of edge sites (see Fig. 7) provides more insight into these results. Here again, k remains effectively constant with different fraction of edge sites. The scatter in the data presented in Figs. 5–7 is mainly attributable to the calculation of f_e , which contributes to the error in both the x - and y -axis. Nevertheless, these results are consistent with earlier studies that invoked the concept that active sites are involved in the oxidation of carbon.

The reaction mechanism between carbon and oxygen is more complex than indicated here, as noted by Radovic and co-workers [14] and Ong [15]. Intermediate species containing chemisorbed molecular (CO_2) and atomic (CO) species may be involved in the reaction pathway. The role of specific surface sites on graphite oxidation is provided by the optical and electron microscopy studies by Thomas [16,17] and Rodriguez-Reinoso and Thrower [18]. More recently,

Henschke et al. [19] used scanning tunneling microscopy to investigate the microstructural changes to graphite surfaces during oxidation. These microscopy studies have provided direct evidence for the higher reactivity of edge and defect sites compared to the basal plane. The observation that k is a constant in Figs. 5, 6b and 7 strongly suggests that the edge sites play a significant role in the oxidation kinetics with flake-like natural graphite particles. This conclusion is consistent with the microscopy studies and the trend that the oxidation kinetics of carbonaceous materials decreases with a decrease in surface area, and active surface area, which occurs during heat treatment.

Acknowledgements

The authors would like to acknowledge the support of HydroQuebec and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Advanced Automotive Technologies of the US Department of Energy under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

References

- [1] E. Charsley, J. Dunn, Rubber Chem. Technol. 55 (1982) 382.
- [2] A. Kirshenbaum, Thermochim. Acta 18 (1977) 113.

- [3] T. Honda, T. Saito, Y. Horiguchi, *Tanso* 72 (1972) 14.
 [4] W. Rubak, H. Karcz, M. Zembruski, *Fuel* 63 (1984) 488.
 [5] L. Radovic, P. Walker, R. Jenkins, *Fuel* 62 (1983) 849.
 [6] N. Laine, F. Vastola, P. Walker, *J. Phys. Chem.* 67 (1963) 2030.
 [7] M. Coltharp, N. Hackerman, *J. Phys. Chem.* 72 (1968) 1171.
 [8] S. Barton, B. Harrison, *J. Chem. Soc. London* 69 (1973) 1039.
 [9] G.-C. Chung, S.-H. Jun, K.-Y. Lee, M.-H. Kim, *J. Electrochem. Soc.* 146 (1999) 1664.
 [10] W. Jiang, G. Nadeau, K. Zaghib, K. Kinoshita, *Thermochim. Acta* 351 (2000) 85.
 [11] K. Zaghib, G. Nadeau, K. Kinoshita, *J. Electrochem. Soc.* 147 (2000) 2110.
 [12] F. Lang, P. Magnier, in: P. Walker (Ed.), *Chemistry and Physics of Carbon*, Vol. 3, Marcel Dekker, New York, 1968, p. 121.
 [13] Recent Carbon Technology, in: T. Ishikawa, T. Nagaoki (Eds.), JEC Press Inc., Cleveland, OH, 1983, p. 123.
 [14] L. Radovic, A. Lizzio, H. Jiang, in: J. Lahaye, P. Ehrburger (Eds.), *Fundamental Issues in Control of Carbon Gasification Reactivity*, Kluwer Academic Publishers, Dordrecht, Germany, 1991, p. 235.
 [15] J. Ong, *Carbon* 2 (1964) 281.
 [16] J. Thomas, in: P. Walker (Ed.), *Chemistry and Physics of Carbon*, Vol. 1, Marcel Dekker, New York, 1966, p. 121. *Carbon* 7 (1969) 359 (reprint).
 [17] G. Hughes, J. Thomas, *Nature* 193 (1962) 838.
 [18] F. Rodriguez-Reinoso, P. Thrower, *Carbon* 12 (1974) 269.
 [19] B. Henschke, H. Schubert, J. Blöcker, F. Atamny, R. Schlögl, *Thermochim. Acta* 234 (1994) 53.

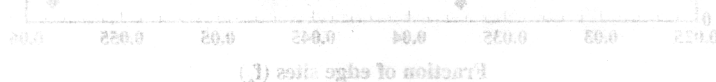


Fig. 7. Relationship between k and the fraction of edge sites on flake-like natural graphite. The circles are the mean of data.

Henschke et al. [19] used scanning tunneling microscopy to investigate the microstructural changes to graphite surfaces during oxidation. These microscopy studies have provided direct evidence for the higher reactivity of edge and defect sites compared to the basal plane. The observation that k is a constant in Figs. 2, 6b and 7 strongly suggests that the edge sites play a significant role in the oxidation kinetics with flake-like natural graphite particles. This conclusion is consistent with the microscopy studies and the trend that the oxidation kinetics of carbonaceous materials decreases with a decrease in surface area and active surface area, which occurs during heat treatment.

Acknowledgements

The authors would like to acknowledge the support of HydroQuebec and the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Advanced Automotive Technologies of the US Department of Energy under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

References

- [1] E. Garsky, *J. Appl. Polym. Sci.* 35 (1988) 383.
 [2] A. Kuchshinov, *Thermochim. Acta* 18 (1977) 117.

surface area increases, the surface area associated with both the edge and basal plane sites also increases. Thus it is not easy to discern if the edge sites are playing a major role in the oxidation kinetics. When the oxidation reaction is assumed to occur mainly on the edge sites, and the kinetic data is normalized for the surface area of edge sites (k_s), the results for k_s as a function of the BET surface area in Fig. 6b are obtained. The trend lines suggest that k_s is constant independent of the BET surface area. This trend is expected for oxidation reactions that are correlated to the surface area of the edge sites. Analysis of the relationship between k and the fraction of edge sites (see Fig. 7) provides more insight into these results. Here again, k remains effectively constant with different fraction of edge sites. The scatter in the data presented in Figs. 2–7 is mainly attributable to the calculation of k_s which contributes to the error in both the x and y -axis. Nevertheless, these results are consistent with earlier studies that invoked the concept that active sites are involved in the oxidation of carbon.

The reaction mechanism between carbon and oxygen is more complex than indicated here, as noted by Radovic and co-workers [14] and Ong [15]. Intermediate species containing chemisorbed molecular (CO_2) and atomic (CO) species may be involved in the reaction pathway. The role of specific surface sites on graphite oxidation is provided by the optical and electron microscopy studies by Thomas [16,17] and Rodriguez-Reinoso and Thrower [18]. More recently,